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Carbonyls in Oxidizing Fat. IV. The Role of Various Fatty Acid Components in Carbonyl Generation

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SUMMARY

Volatile monocarbonyls produced by mildly oxidized esters of oleic, linoleic, linolenic acids and fats have been characterized by paper chromatography of 2,4-dinitrophenylhydrazone derivatives. The unsaturated fatty acid esters yielded a total of 7 *n*-alkanals, 8 *n*-alk-2-enals, and 4 alk-2,4-dienals; and similar results were obtained with the fats. Each unsaturated acid produced three major characteristic aldehydes. Comparisons of esters and glycerides showed the presence of keto or aldehyde ester scission products.

Fats become rancid at widely varying eroxide levels (Dugan, 1959; Lea, 1953; ips, 1952; Nikkila and Linko, 1955). This true, to a smaller degree, even in fats of e same kind (Chipault *et al.*, 1945; Gad-is *et al.*, 1959; Naumann *et al.*, 1951). Con-equently, peroxide numbers are of little pecific value as indices of oxidative ran-idity. Similarly total carbonyl values ap-ear to be of limited use (Gaddis *et al.*, 959). Although other factors (Chipault *al.*, 1945; Dugan, 1959; Watts and Wong, 951) are unquestionably involved, a pri-ary factor would presumably be due to fferences in fatty acid composition, with sulting variation in the kind and amount carbonyls produced.

A considerable amount of work (Gaddis *al.*, 1959; Lea *et al.*, 1953; Morris, 1954) as been done over the years on the volatile rbonyls formed by autoxidized unsatu-ated fatty acid esters and various animal nd vegetable fats. For the most part, oxi-ation has been considerably beyond the oint of rancidity, and, because of inade-uate methods, analyses have been incom-lete.

This work applied newly developed micro-methods (Ellis and Gaddis, 1959; Ellis *et al.*, 1958; Gaddis and Ellis, 1957, 1959 a, b; addis *et al.*, 1959, 1960) to qualitative de-rmination of the volatile monocarbonyls oduced from mildly oxidized esters of oleic, linoleic, and linolenic acids, and animal and vegetable fats.

MATERIALS AND METHODS

Methyl stearate, methyl palmitate, methyl oleate, and ethyl linoleate were furnished by Dr. H. B. Knight, of our Eastern Regional Laboratory. Edible-grade refined palm oil (fruitcoat) was furnished by Dr. V. K. Babayan, of E. F. Drew and Company, Inc. Highly purified oleate triglyceride and methyl linolenate were obtained from The Hormel Foundation, Austin, Minnesota. Pork, beef, and lamb fats were steam-rendered, and stored in vacuum-packed cans at −30°F. until required. Cocoa butter and linseed oil were purchased from a chemical company. Soybean and peanut oils were obtained from reliable commercial sources.

Twenty-five grams of esters (8 g methyl linolenate), 25 g of mixtures of esters, and 25 g of the fats were oxidized in thin films in 11-cm-diameter containers by ultraviolet light at room temperature (28–30°C). Peroxide values were followed on 0.200 g samples by the method of Kenaston *et al.* (1955). Steam-volatile carbonyl 2,4-dinitrophenylhydrazones (2,4-DNPH) were isolated from 2–10 g unheated and heated (165°C for 15 minutes) samples by methods described by Gaddis *et al.* (1959). Volatile carbonyl 2,4-DNPH's were separated into mono- and dicarbonyl derivatives by methods described earlier (Gaddis and Ellis, 1959 b; Gaddis *et al.*, 1959, 1960). Non-volatile and bound carbonyls remaining in the steam distillation residues were isolated by reaction with Girard T reagent and Dowex 50 cation resin at room temperature (Gaddis *et al.*, 1960). Carbonyl 2,4-DNPH's isolated by the Girard T reagent were fractionated into volatile and nonvolatile mono- and dicarbonyl groups (Gaddis *et al.*, 1960). Steam-volatile monocarbonyls were separated into classes, and the classes resolved into individual compounds that were identified by previously reported methods and applications (Ellis and Gaddis, 1959; Ellis *et al.*, 1958; Gaddis and Ellis, 1957, 1959 a, b; Gaddis *et al.*, 1959). Total determinable carbonyls were measured by the method of Henick *et al.* (1954), Gaddis *et al.*, (1960). Iodine values were measured by the Wijs method (Official and Tentative Methods of the Am. Oil Chemists' Soc., 1954).

Methyl oleate, trioleate glyceride, and ethyl linoleate were oxidized separately and simultaneously. Amounts of oxidation permitted were such as to give a combined peroxide value of about 30 for mixtures of the two unsaturated acids commonly found in pork, beef, and lamb fat. Similarly, mixtures of methyl palmitate, stearate, oleate, and ethyl linoleate corresponding to the three animal fats were oxidized to peroxide values of about 30. Methyl linolenate was oxidized to a peroxide level of 93. No attempt was made to synchronize oxidation of this ester with that of the others, since it is ordinarily present in most animal fats in very small quantities. Finally, eight animal and vegetable fats of widely varying fatty acid composition were oxidized to peroxide values in the region of 30.

RESULTS AND DISCUSSION

The primary purpose of this paper was to report the effect of fatty acid composition on the kind of volatile monocarbonyls generated by oxidation. However, considerable quantitative data have been accumulated in the process, and it seems appropriate to give a brief account of some of the more significant findings.

Unheated and heated steam-volatile carbonyls from the mixtures of fatty acid esters, based on total determinable carbonyl content (Gaddis *et al.*, 1959; Henick *et al.*, 1954), were considerably higher than those obtained from oxidized pork fat (4% and 19% greater, respectively) (Gaddis *et al.*, 1960). Similarly, the trioleate glyceride yielded a much lower amount of volatile carbonyl than the simultaneously and equally oxidized methyl oleate. The methyl oleate contained 0.8% polyunsaturate impurities that may have influenced the course of oxidation. However, it would be expected that some scission fragments, such as keto or aldehyde acid, would be volatile in the case of the esters and should show up mostly in the "dicarbonyl" fraction. This was clearly indicated in comparison of the volatile "dicarbonyl" fractions from methyl oleate, trioleate glyceride, and mixtures of fatty acid esters. An interesting observation was that the volatile "dicarbonyl" fractions of the fatty acid esters, mixtures thereof, and also the trioleate glyceride increased greatly on heating. This was quite different from the behavior of the "dicarbonyl" fraction of beef, lamb, and pork tissue and rendered fat (Gaddis and Ellis, 1959b; Gaddis *et al.*, 1959, 1960), which showed little quantitative change. The presence of volatile carbonyl-acid fragments may not account for all of the differences since the percentage of monocarbonyls was also much higher. The differences are evidently related to retention of carboxyl carbonyls, and possibly the presence of some other kind of binding in the glyceride structure. Some of these bound and nonvolatile forms are doubtless isolated by the Girard T reagent (Gaddis *et al.*, 1960). The nonvolatile carbonyls are the major fraction, and are of considerable interest for a number of reasons (Berry and McKerrigan, 1958; Gaddis *et al.*, 1960). Evidence was unmistakable that much of the total determinable carbonyls are present in bound forms (Gaddis *et al.*, 1960). The distribution of volatile and nonvolatile mono- and dicarbonyl fractions isolated by the Girard T reagent from methyl oleate and ethyl linoleate was similar (Gaddis *et al.*, 1960). The distribution of the Girard T fractions from linolenate, however, was quite different. Linolenate volatile carbonyls isolated by the Girard T reagent were 65% of the total, and high-molecular-weight polycarbonyls were 90% of the nonvolatile fraction. Fugger *et al.* (1951) found that there was marked difference in the course of linolenate oxidation compared to that of oleate and linoleate. Scission and polymerization occurred immediately upon oxidation of linolenate.

Table 1 shows determinations of micromoles of volatile monocarbonyls per 10 g material for methyl oleate, trioleate glyceride, ethyl linoleate, and methyl linolenate

Table 1. Total monocarbonyl values of oxidized :ters.[a]

	Peroxide	Monocarbonyl 2,4-dinitrophenylhydrazones Micromoles per 10 g Total	Per cent Alkanal	Enal	Dienal
ethyl oleate	40.8	7.63	58.2	41.8	
		35.72	29.9	70.1	
ethyl oleate	52.0	7.12	61.8	38.2	
		49.63	28.1	71.9	
ethyl oleate	71.0	15.79	60.9	39.1	
		54.89	32.7	67.3	
rioleate	43.0	4.86	60.1	39.9	
		30.12	27.4	72.6	
·ioleate	52.0	4.94	59.7	40.3	
		26.85	32.3	67.7	
·ioleate	80.0	6.93	54.4	45.3	
		......	......	......	
hyl linoleate	200.0	16.87	52.3	23.5	24.2
		109.56	11.5	16.3	72.2
hyl linoleate	336.0	29.04	52.7	19.6	27.7
		125.15	14.5	19.4	66.1
hyl linoleate	536.00	53.43	57.9	19.1	23.0
		172.01	24.3	12.2	63.5
ethyl linoleate	93.3	8.35	43.4	24.0	32.6
		27.77	12.4	15.4	72.2

[a] The first of each pair of lines is for unheated; : second is for heated.

the methyl oleate and trioleate, the pro- rtions of alkanal were greater than those alk-2-enal, though the latter increased nsiderably upon heating. In the ethyl oleate and methyl linolenate, the alk-2,4- :nal class increased greatly when exposed heat. Since both of these polyene acids, will be shown later, generate low-molecu- -weight alkanals and alk-2-enals, an ap- :ciable loss of these compounds probably ·k place when heated (Gaddis *et al.*, 59). Also, the alk-2-enal class is in error the extent of the amount of alkanal C_2 :sent, since that compound separates with t class (Gaddis and Ellis, 1959a, b).

Table 2 compares quantitative monocar- ıyl class data for oxidized pork, lamb, and f rendered fat, mixtures of palmitic, ıric, oleic, and linoleic ester, and calcu- ·d combinations of data from separately dized oleic and linoleic esters. The mix- es were made up as follows: pork— :hyl palmitate 30.1%, methyl stearate 2%, methyl oleate 46.6%, and ethyl linoleate 7.1%; lamb—24.4%, 34.5%, 39.1%, and 2.0%, respectively; and beef—32.0%, 21.0%, 45.9%, and 1.1%, respectively. These are about average compositions for the three fats, but not necessarily the composition of the fats examined. Unheated proportions of classes were similar. In the heated samples, the proportions of class were about the same for the mixtures and fats. However, calculated data gave much lower proportions of alkanals and higher proportions of alk-2-enals. The total amount of monocarbonyls also was much higher in the calculated samples. Apparently the release of volatile monocarbonyls was greater in separately oxidized unsaturated acids than when they were mixed. Possibly, more polymerization took place in the mixtures.

Table 3 shows quantitative class data for animal fats and vegetable oils oxidized to approximately the same peroxide values. The data are arranged in the order of increasing linoleic and linolenic acid content. Except for linseed oil, which was initially

Table 2. Total monocarbonyl values of ester mixtures and fats.[a]

	Peroxide	Monocarbonyl 2,4-dinitrophenylhydrazones Micromoles per 10 g Total	Per cent Alkanal	Enal	Dienal
Pork fat mixture	28.0	4.34	61.8	28.8	9.4
		10.63	39.0	36.6	24.4
Pork fat	31.0	3.50	63.4	24.0	12.6
		9.64	35.4	27.8	36.8
Pork fat comb. (calculated)	33.2	4.76	56.7	37.2	6.1
		24.42	24.1	52.9	23.0
Lamb fat mixture	31.0	5.87	59.3	33.4	7.3
		12.36	51.5	38.3	10.2
Lamb fat	30.0	4.76	53.8	41.4	4.8
		10.31	51.5	39.7	8.8
Lamb fat comb. (calculated)	27.1	3.94	59.1	32.7	8.2
		21.90	36.5	65.9	7.6
Beef fat mixture	33.0	3.93	62.3	30.3	7.4
		15.49	43.6	47.6	8.8
Beef fat	31.5	4.73	62.2	30.0	7.8
		10.31	49.2	41.6	8.9
Beef fat comb. (calculated)	27.6	3.91	60.4	35.0	4.6
		24.16	27.3	68.9	3.8

[a] The first of each pair of lines is for unheated; the second is for heated.

Table 3. Carbonyl values of oxidized fats and oils.[a]

	Iodine value	Peroxide	Total determinable absorbance λ max	Carbonyl 2,4-dinitrophenylhydrazones: Volatile monocarbonyl: Micromoles per 10 g: Total	Dienal	Per cent: Alkanal	Enal	Dienal
Beef	38.7	31.5	48.6	4.73	0.29	62.2	30.0	7.8
				10.31	1.35	49.5	41.6	8.9
Lamb	36.5	30.0	51.5	4.76	0.23	53.8	41.4	4.8
				10.31	0.91	51.5	39.7	8.8
Cocoa butter	38.3	33.0	47.3	3.00	0.35	64.0	24.3	11.7
				5.52	0.60	56.1	33.0	10.9
Pork	58.8	30.8	40.3	3.50	0.44	63.4	24.0	12.6
				9.64	3.55	35.4	27.8	36.8
Palm oil	55.9	27.0	26.5	2.61	0.29	69.7	19.2	11.1
				5.86	0.82	58.4	27.6	14.0
Peanut oil	104.9	26.0	29.8	2.20	0.41	55.5	23.6	20.9
				5.85	1.79	46.0	30.6	23.4
Soybean oil	136.1	29.3	19.9	1.43	0.18	63.6	23.7	12.7
				4.28	1.77	30.8	27.8	41.4
Linseed oil	181.0	33.0	50.4	10.45	3.33	44.0	23.6	32.4
				16.13	7.55	30.5	22.7	46.8

[a] The first of each pair of lines is for unheated; the second is for heated.

in poor condition, the total determinable carbonyl value (Gaddis *et al.*, 1960; Henick *et al.*, 1954) and monocarbonyls in general tended to decrease with increase in iodine values and polyene acids. However, the vegetable oils, two of which (cocoa butter and palm oil) are similar in composition to lamb and pork fat, were invariably lower in most of these values than the animal fats, and appeared to be in a separate group. It is therefore difficult to say at this time whether this is due to the presence of antioxidants in the vegetable oils or the higher content of polyene acids. In most cases, the percentage of alk-2,4-dienal class increased with total unsaturation and polyene acid content. Perhaps the most striking difference was in the pork fat. This showed a much greater increase in alk-2,4-dienals upon heating than other fats of the same or much higher polyene fatty acid content. Palm oil has a composition very similar to that of pork fat, but showed little change in proportion of dienals. The proportion of dienal obtained from pork fat was higher than that obtained from peanut oil, and almost as high as that from soybean oil. Peanut oil has four times as much linoleic acid, and soybean oil has seven times as much linoleic and 30 times as much linolenic acid. The extreme vulnerability of pork fat to rancidity is difficult to explain on the basis of its polyunsaturated acid content. While the above differences may be due entirely to the action of antioxidants, the possible effect of differences in glyceride structure seems worth considering. Mattson and Lutton (1958) have observed that pork fat has a unique triglyceride structure. The unsaturated acids are predominantly in the 1 and 3 positions. Beef, lamb, and vegetable oils have most of the saturated acids positioned in the 1 and 3 positions. It would seem that unsaturated acids would be more accessible to oxidation in the 1 and 3 positions than in the 2 position. This might explain the relatively much higher yield of alk-2,4-dienals from pork fat. The possibility seems worthy of further investigation.

Volatile monocarbonyls identified from methyl oleate, ethyl linoleate, and methyl linolenate are shown in Table 4. Trace and

Table 4. Volatile monocarbonyls identified in oxidized unsaturated esters.[a]

	n-Alkanals	Enals	Dienals
Methyl oleate	C_6*		
	C_8		
	$C_9\Delta$	C_9*	Trace
		$C_{10}\Delta$	
	C_{11}	$C_{11}\Delta$	
Ethyl linoleate	C_2		
	C_3	C_6*	
	$C_6\Delta$	$C_7\Delta$	
		C_8	
	C_9*	C_9	C_9*
		C_{10}*	$C_{10}\Delta$
		C_{11}*	
Methyl linolenate	C_2		
	$C_3\Delta$		
	C_4	C_4	
		$C_5\Delta$	
		C_6	$C_7\Delta$
		C_7	C_9*
		C_9*	

[a] *trace; Δ major.

major compounds are indicated. Some of the trace compounds probably result from impurities. The methyl oleate sample contained 0.8% polyunsaturates. The trace compounds tended to increase with degree of oxidation. In the most highly oxidized oleate sample, a trace of alk-2,4-dienal class was observed. Trace *n*-alkanal C_6 probably comes from linoleate. It might at first appear that trace *n*-alk-2-enal C_9 would come from linoleate, but if that were the case, the major alk-2-enal C_7 should also be present.

Little has been reported concerning the identity of the volatile monocarbonyls produced by oxidized oleate. Swift *et al.* (1948) isolated alk-2-enal C_{11} from heated oleate hydroperoxide. Bickford *et al.* (1948) found C_8, C_9, C_{10}, and C_{11} isomeric hydroperoxides formed in oxidized oleic acid. These would yield *n*-alk-2-enals C_{11} and C_{10} and *n*-alkanals C_9 and C_8.

The ethyl linoleate used was 97–98% pure and had an iodine value of 164.9. Trace compounds alkanal C_9 and alk-2-enals C_{10} and C_{11} probably come from oleate impurity. Trace alk-2-enal C_6 could come from linolenate, but may not have, because the major linolenate alk-2-enal C_5 should also be present. Chang and Kummerow (1953) found *n*-alkanals C_3, C_5, and C_6 among the volatile decomposition products of linoleate oxidative polymers. The compound *n*-alkanal C_5 was not detected in this study. Recently, Patton *et al.* (1959) isolated alkanal C_6, alk-2-enal C_7, C_9, and C_{10}, and alk-2,4-dienal C_{10} from heated methyl linoleate. Badings (1959) found alkanal C_2, alk-2-enal C_8, and alk-2,4-dienal C_{10} in oxidized ammonium linoleate.

The highly purified methyl linolenate yielded no trace compounds that could be logically traced to the other two unsaturated fatty esters. Kawahara *et al.* (1952) found alkanal C_2 and C_3 and alk-2-enal C_5 among the volatile cleavage products of oxidized linolenate. Johnson *et al.* (1953) found methyl ethyl ketone, alkanal C_2 and C_3, and alk-2-enal C_5 in the products of decomposed oxidative polymers of linolenate.

Table 5. Volatile monocarbonyls identified in oxidized mixtures of fatty acid esters.[a]

	Alkanal	Alkenal	Dienal
Pork mixture	C_2		
fatty acid esters	$C_6\Delta$		
		$C_7\Delta$	
	C_8	C_8	
	$C_9\Delta$	C_9	C_9
		$C_{10}\Delta$	$C_{10}\Delta$
	C_{11}	$C_{11}\Delta$	
			C_{12}*
Beef mixture	C_2		
fatty acid esters	C_6		
		C_7	
	C_8	C_8	
	$C_9\Delta$	C_9	C_9
		$C_{10}\Delta$	$C_{10}\Delta$
	C_{11}	$C_{11}\Delta$	
			C_{12}*
Lamb mixture	C_2		
fatty acid esters	C_6		
		C_7	
	C_8	C_8	
	$C_9\Delta$	C_9	C_9
		$C_{10}\Delta$	$C_{10}\Delta$
	$C_{11}\Delta$	$C_{11}\Delta$	
			C_{12}*

[a] *trace; Δ major.

A compound of an apparently new class was detected in small amounts in the oxidized linolenate. This separated in paper chromatography (Gaddis and Ellis, 1959a, b) slightly below the alk-2,4-dienal class, had a maximum of 390 mμ in CCl_4, and a probable carbon chain length of C_9 to C_{11}. This compound might be an alk-2,4,6-trienal (Braude and Jones, 1945; Nazarov *et al.*, 1957). A deca-2,4,6-trienal could be formed by scission of a 9-hydroperoxide of linolenate. This fraction requires further study.

Based on the above findings, an oxidized mixture of the three unsaturated fatty acids would be expected to produce the following volatile monocarbonyls: *n*-alkanals C_2, C_3, C_4, C_6, C_8, C_9, and C_{11}; *n*-alk-2-enals C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, and C_{11}; and *n*-alk-2,4-dienals C_7, C_9, and C_{10}. Volatile monocarbonyls found in oxidized mixtures of stearic, palmitic, oleic, and linoleate are shown in Table 5. The expected compounds were found, with minor exceptions: alkanals C_3 was not found. A tentative alk-2,4-dienal trace C_{12} was detected repeatedly.

Compounds found in the 8 fats and oils are shown in Table 6. Qualitative differences were as might be predicted from the composition. Over-all, there was a remarkable qualitative similarity. As indicated by variations in major compounds, and the previously discussed differences in class proportions, there were obviously great quantitative differences between fats. Tentative

Table 6. Volatile monocarbonyls identified in oxidized fats and oils.[a]

	n-Alkanals	Enals	Dienals
Pork fat	C_2*		
	C_3		
	$C_6\Delta$		
		C_7	C_7
	C_8*	C_8	
	$C_9\Delta$	C_9	C_9
		C_{10}	$C_{10}\Delta$
	C_{11}*	C_{11}	
			C_{12}*
Beef fat	C_2*		
	C_3*		
	C_6		
	C_7	C_7	C_7
	C_8	C_8	
	C_9	$C_9\Delta$	C_9*
	C_{10}	$C_{10}\Delta$	C_{10}
	C_{11}*	$C_{11}\Delta$	C_{11}
			C_{12}*
Lamb fat	C_6		
	C_7	C_7*	C_7
	C_8*	C_8*	
	$C_9\Delta$	$C_9\Delta$	C_9*
	C_{10}	$C_{10}\Delta$	C_{10}
	C_{11}	$C_{11}\Delta$	
			C_{12}*
Peanut oil	$C_6\Delta$		
		$C_7\Delta$	C_7
	C_8	$C_8\Delta$	
	C_9	$C_9\Delta$	C_9
		C_{10}*	$C_{10}\Delta$
	C_{11}	C_{11}*	
			C_{12}*
Palm oil	$C_6\Delta$		
		C_7	C_7
	C_8	C_8	
	C_9	C_9	C_9
		C_{10}	$C_{10}\Delta$
	C_{11}	C_{11}	
	C_{12}*		C_{12}*
Linseed oil	C_2		
	$C_3\Delta$		
	C_4	C_4	
		$C_5\Delta$	
	$C_6\Delta$	$C_6\Delta$	
		$C_7\Delta$	$C_7\Delta$
	C_9	C_9	C_9
			C_{10}
Cocoa butter	$C_6\Delta$		
		C_7	C_7
	C_8	C_8	
	$C_9\Delta$	C_9	C_9
		$C_{10}\Delta$	$C_{10}\Delta$
	C_{11}*	C_{11}	
			C_{12}*
Soybean oil	C_2*		
	C_3		
		C_5	
	$C_6\Delta$	C_6	
		$C_7\Delta$	$C_7\Delta$
		C_8	
	C_9	$C_9\Delta$	C_9
		C_{10}	$C_{10}\Delta$
		C_{11}	
			C_{12}*

[a] *trace; Δmajor.

lk-2,4-dienal trace C_{12}, found in the fatty cid ester mixtures, also appears here. Alkaal C_7 and C_{10} were detected in beef and mb fat. It will be noted that alk-2,4-dienal C_7, which is characteristic of linolenate, apears in beef, pork, and lamb, although that cid is almost a trace component in those its.

Gaddis and Ellis (1959b) found that hexnal was the major volatile monocarbonyl n pork tissue fat oxidized at low temperaure. However, the above data on rendered ork fat indicate that alkanal C_9 was equally bundant. Alkanal C_9 comes from oleate, nd C_6 from linoleate. This is in line with he observation of Watts and Wong (1951) hat hemoglobin oxidizes linoleic and linoenic acids selectively. The action of catalysts, enzymes (Koch *et al.*, 1959), and prond antioxidants, and the conditions of oxilation may have considerable influence on he qualitative and quantitative nature of he volatile monocarbonyls. Slover and Dugan (1957) found that gamma irradiation of oleate caused no significant departure rom unirradiated autoxidation. However, Witting and Schweigert (1958) found alk-2,4-dienal C_{11} to be the predominant caronyl from lard oxidized by gamma irradiaion. This compound was observed by Gaddis and Ellis (1959b) as a minor comonent in oxidized pork tissue fat. However, it was not observed in the present work except in beef tallow. The major inoleate dienal was C_{10}. Witting and Schweigert (1958) comment on the variaion of the principal dienal linoleate degradaion products in different fats. They also ound alkanals C_3, C_4, C_5, C_6, C_9, and C_{10} nd alk-2-enals C_3 and C_4. Pippen *et al.* (1958) found acetone and methyl ethyl ketone (Gaddis and Ellis, 1957); alkanals C_2, C_3, C_4, C_5, C_6, C_8, and C_9; alk-2-enals C_5, C_6, C_7, C_{10}, and C_{11}; and alk-2,4-dienal C_7. We have not detected alkanal C_5 or alk-2-enal C_3. Traces of the latter might be missed in our systems, since it forms mixtures with alkanal C_2. The new class of monocarbonyl (a possible trienal), found in linolenate, was also detected in linseed oil.

Heating the esters or fats at 165° did not affect the qualitative composition of the volatile monocarbonyls, although in some instances small amounts of low-molecular-weight products were lost through volatilization (Gaddis *et al.*, 1959). There were large increases in volatile monocarbonyls, and doubtless large changes in relative amounts of the individual compounds similar to those shown for pork tissue fat by Gaddis and Ellis (1959b).

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REFERENCES

Badings, H. T., 1959. Isolation and identification of carbonyl compounds formed by autoxidation of ammonium linoleate. *J. Am. Oil Chemists' Soc.* **36**, 648.

Berry, N. W., and A. A. McKerrigan, 1958. Carbonyl compounds as a criterion of flavor deterioration in edible fats. *J. Sci. Food Agr.* **9**, 694.

Bickford, W. G., G. S. Fisher, L. Kyame, and C. E. Swift, 1948. Autoxidation of fats. II. Preparation and oxidation of methyl oleate-maleic anhydrine adduct. *J. Am. Oil Chemists' Soc.* **25**, 254.

Braude, E. A., and E. R. H. Jones, 1945. Studies in light absorption. II. 2,4-Dinitrophenylhydrazones. *J. Chem. Soc.* **382**, (84), 498.

Chang, S., and F. A. Kummerow, 1953. The volatile decomposition products and the organoleptic characteristics of the oxidative polymers of ethyl linoleate. *J. Am. Oil Chemists' Soc.* **30**, 251.

Chipault, L. R., W. O. Lundberg, and G. O. Burr, 1945. The chemical determination of tocopherols in animal fats; the stability of hog fats in relation to fatty acid composition and tocopherol contents. *Arch. Biochem.* **8**, 321.

Dugan, L. R., 1959. Antioxidants. *Am. Perfumer Aromat.* **73**, 47.

Ellis, R., and A. M. Gaddis, 1959. Paper chromatography of 2,4-dinitrophenylhydrazones. Estimation of 2-alkanone, n-alkanal, alk-2-enal and alk-2,4-dienal derivatives. *Anal. Chem.* **31**, 1997.

Ellis, R., A. M. Gaddis, and G. T. Currie, 1958. Paper chromatography of 2,4-dinitrophenylhydrazones of saturated aldehydes. *Anal. Chem.* **30**, 475.

Fugger, J., J. A. Cannon, K. T. Zilch, and H. J. Dutton, 1951. Analysis of fat oxidation products by counter current distribution methods.

III. Methyl linolenate. *J. Am. Oil Chemists' Soc.* **28**, 285.

Gaddis, A. M., and R. Ellis, 1957. Volatile saturated aldehydes in rancid fat. *Science* **126**, 745.

Gaddis, A. M., and R. Ellis, 1959 a. Paper chromatography of 2,4-dinitrophenylhydrazones. The resolution of 2-alkanone, alkanal, alk-2-enal, and alk-2,4-dienal derivatives. *Anal. Chem.* **31**, 870.

Gaddis, A. M., and R. Ellis, 1959 b. Carbonyls in oxidizing fat. II. The identity and amounts of steam volatile carbonyls in a rancid freezer stored pork fat. *Food Research* **24**, 392.

Gaddis, A. M., R. Ellis, and G. T. Currie, 1959. Carbonyls in oxidizing fat. I. Separation of steam volatile monocarbonyls into classes. *Food Research* **24**, 283.

Gaddis, A. M., R. Ellis, and G. T. Currie, 1960. Carbonyls in oxidizing fats. III. The distribution of volatile and non-volatile carbonyls. *Food Research* **25**, 506.

Henick, A. S., M. F. Benca, and J. H. Mitchell, 1954. Estimating carbonyl compounds in rancid fats and foods. *J. Am. Oil Chemists' Soc.* **31**, 88.

Johnson, O. C., S. S. Chang, and F. A. Kummerow, 1953. Volatile decomposition products of the oxidative polymers of ethyl linolenate. *J. Am. Oil Chemists' Soc.* **30**, 317.

Kawahara, F. K., H. J. Dutton, and J. C. Cowan, 1952. Volatile cleavage products of autoxidized methyl linolenate. *J. Am. Oil Chemists' Soc.* **29**, 633.

Kenaston, C. B., K. M. Wilbur, A. Ottolenghi, and F. Bernheim, 1955. Comparison of methods for determining fatty acid oxidation produced by ultraviolet irradiation. *J. Am. Oil Chemists' Soc.* **32**, 33.

Koch, R. B., J. W. Smull, A. S. Henick, and D. H. Calloway, 1959. Comparison of lipoxidase oxidation and autoxidation of cotton seed oil. *J. Am. Oil Chemists' Soc.* **36**, 205.

Lea, C. H., 1953. Recent developments in the study of oxidative deterioration of lipids. *Chem. & Ind.* (London) **41**, 1303.

Lips, H. J., 1952. Oxidative flavor deterioration in fats and oils. *Food in Canada* **9** (June).

Mattson, F. H., and E. S. Lutton, 1958. The specific distribution of fatty acids in the glycerides of animal and vegetable fats. *J. Biol. Chem.* **233**, 868.

Morris, S. G., 1954. Fat rancidity. Recent studies on the mechanism of fat oxidation in relation to rancidity. *J. Agr. Food Chem.* **2**, 126.

Naumann, H. D., D. E. Brady, A. Z. Palmer, and L. N. Tucker, 1951. Odor, flavor, and peroxide value as measures of rancidity in frozen ground pork. *Food Technol.* **5**, 496.

Nazarov, I. N., L. A. Kazitsyna, and I. I. Zaretskaya, 1957. Study of the absorption spectra of 2,4-dinitrophenylhydrazones. *Zhur. Obshcheĭ. Khim.* **27**, (3), 606.

Nikkila, O. E., and R. R. Linko, 1955. Comparison of tests for oxidative rancidity in edible oils. *Suomen Kemistilehti* **28**B, 113.

Official and Tentative Methods of the American Oil Chemists' Society. 1954.

Pattón, S., I. J. Barnes, and L. E. Evans, 1959. n-Deca-2,4-dienal, its origin from linoleate and flavor significance in fats. *J. Am. Oil Chemists' Soc.* **36**, 280.

Pippen, E. L., M. Nonaka, F. F. Jones, and F. Stitt, 1958. Volatile compounds of cooked chicken. I. Compounds of cooked chicken. I. Compounds obtained by air entrainment. *Food Research* **23**, 103.

Slover, H. T., and L. R. Dugan, Jr., 1957. Influence of high energy radiation on the oxidation of oleic acid and methyl oleate. II. Sites of oxygen attack. *J. Am. Oil Chemists' Soc.* **34**, 333.

Swift, C. E., F. G. Dollear, L. E. Brown, and R. T. O'Connor, 1948. Decomposition of methyl hydroperoxide oleate. *J. Am. Oil Chemists' Soc.* **25**, 39.

Watts, B. M., and R. Wong, 1951. Some factors affecting the antioxidant behavior of scorbic acid with unsaturated fats. *Arch. Biochem.* **30**, 110.

Witting, L. A., and B. S. Schweigert, 1958. A characterization of volatile carbonyl compounds isolated from meat fat subjected to gamma radiation. *J. Am. Oil Chemists' Soc.* **35**, 413.